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EPOXY RESIN, EPOXY RESIN COMPOSITION AND CURED PRODUCT THEREOF
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(54) [Title of the Invention]

/1¹

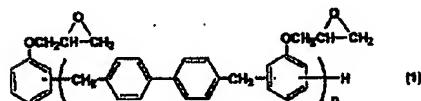
Epoxy Resin, Epoxy Resin Composition and Cured Product Thereof

[Claim(s)]

/2

[Claim 1] An epoxy resin characterized by being represented by the general formula (1):

[Formula 1]



(where n in the formula is an average value denoting a positive number from 0.1 to 6.0),

the ratio A/B of the integrated value A of the peak existing at 35 to 37 ppm and the integrated value B of the peak existing at 40 to 42 ppm, both in the ¹³C-NMR spectrum, being at least 1.45, and the softening point being at least 63°C.

[Claim 2] An epoxy resin composition comprised by containing the epoxy resin of Claim 1 and a curing agent.

[Claim 3] The epoxy resin composition of Claim 2 which contains a curing accelerator.

[Claim 4] A cured product comprised by curing the epoxy resin composition of Claim 2 or 3.

[Claim 5] A varnish comprised by dissolving the epoxy resin composition of Claim 2 or 3 in a solvent.

¹Number in the margin indicates pagination in the foreign text.

[Detailed Specifications]

[0001] [Technical Field of the Invention]

The present invention relates to an epoxy resin which is useful for insulating materials for electrical or electronic parts including those for highly reliable sealing of semiconductors, various composite materials including laminate boards (printed wiring boards) and CFRPs (carbon fiber-reinforced plastics), adhesives, paints, and the like, an epoxy resin composition comprising it, and a cured product thereof.

[0002] [Prior Art]

Epoxy resins are used extensively in fields, such as electrical and electronic parts, materials for manufacturing, adhesives and paints, because of their workability and outstanding electrical characteristics, heat resistance, adhesiveness, moisture resistance (water resistance), etc.

[0003] Even more improvement in the various characteristics, such as heat resistance, moisture resistance, close adhesiveness and low dielectric properties, are demanded due to the growth in the electrical and electronic fields particularly in recent years. In addition, lightweight materials outstanding in mechanical characteristics are demanded as structural materials for aerospace materials, leisure and sports equipment applications, etc. Although many epoxy resins have been proposed for these demands, the solubility of epoxy resins in solvents is poor; hence, problems occurred if they were stored in a state dissolved in a solvent prior to preparing varnishes therefrom because crystal-like deposits were observed, etc.

[0004] [Problems to be Solved by the Invention]

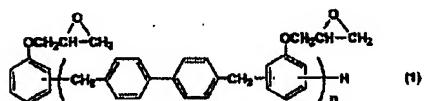
It is an object of the present invention to provide an epoxy resin with outstanding solvent solubility and useful for insulating materials for electrical or electronic parts exhibiting outstanding heat resistance, moisture resistance (water resistance) and low dielectric properties (highly reliable sealing of semiconductors, etc.), various composite materials including laminate boards (printed wiring boards, etc.) and CFRPs, adhesives, paints, and the like, an epoxy resin composition comprising it, and a cured product thereof.

[0005] [Means for Solving the Problems]

As a result of painstaking research on epoxy resins having the characteristics, as mentioned above, the inventors of the present invention completed the present invention. That is, the present invention relates to (1) an epoxy resin characterized by being represented by the general formula (1) :

[0006]

[Formula 2]



[0007] (where n in the formula is an average value denoting a positive number from 0.1 to 6.0), the ratio A/B of the integrated value A of the peak existing at 35 to 37 ppm and the integrated value B of the peak existing at 40 to 42 ppm, both in the $^{13}\text{C-NMR}$ spectrum, being at least 1.45, and the softening point being at least 63°C , (2) an epoxy resin composition comprised by containing the epoxy resin of (1) above and a curing agent,

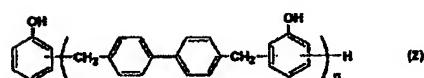
- (3) the epoxy resin composition of (2) above which contains a curing accelerator,
- (4) a cured product comprised by curing the epoxy resin composition of (2) or (3) above, and (5) a varnish comprised by dissolving the epoxy resin composition of (2) or (3) above.

[0008] [Embodiments of the Invention]

The epoxy resin of the present invention is obtained by a glycidylation reaction wherein an epihalohydrin is reacted with a phenol aralkyl resin represented by the Formula (2):

[0009]

[Formula 3]



[0010] (where n is an average value denoting a positive number from 0.1 to 6.0).

the phenol aralkyl resin of Formula (2) in use is obtained by reacting a phenol and a biphenyl derivative shown by the Formula (3), as shown in, e.g., Tokkai No. 8-143648:

[0011]

[Formula 4]



[0012] (where X denotes an alkoxy group).

Moreover, while obtaining the aforesaid phenol aralkyl resin, the proportion of the biphenyl derivative and phenol used may differ depending on the type of solvent when one is used in the reaction, and the A/B of the /3 resulting resin is determined suitably to satisfy the above-mentioned

conditions, and when the reaction is performed without a solvent, even though not indiscriminately put, it is normally 1.1 to 2.9 moles, and preferably, 1.5 to 2.8 moles of phenol to 1 mole of biphenol derivative.

[0013] Although there is epichlorohydrin, epibromhydrin, epiiodohydrin, and the like for the epihalohydrin used in the glycidylation reaction, epichlorohydrin, which is readily procured and inexpensive in the industry, is preferable. This reaction can be performed in accordance with a conventionally-known method.

[0014] For example, a solid of an alkaline metal hydroxide, such as sodium hydroxide or potassium hydroxide, is added to a mixture of the above-mentioned phenol aralkyl resin and epihalohydrin, or reacted for 0.5 to 10 minutes at 20 to 120°C during the addition. In this case, a method in which an aqueous solution of the alkaline metal hydroxide may be used may be employed, and in such a case, this alkaline metal hydroxide is added continuously, and at the same time, in order to distill the water and epichlorohydrin continuously under reduced pressure or under normal pressure from within the reaction mixture, it is separated further and the water is removed, and the epichlorohydrin is returned continuously to the reaction mixture.

[0015] In the above-mentioned method, the amount of the epihalohydrin used per equivalent of hydroxyl groups in the phenyl aralkyl resin normally is 0.5 to 20 moles, and preferably, 0.7 to 10 moles. The amount of the alkaline metal hydroxide moles per equivalent of hydroxyl groups in the phenol aralkyl resin normally is 0.5 to 1.5 moles, and preferably, 0.7 to 1.2. In addition, an epoxy resin having a small amount of a hydrolyzable

solvent, which will be defined later, is obtained by adding an aprotic solvent, such as dimethyl sulfone, dimethyl sulfoxide, dimethyl formamide, or 1,3-dimethyl-2-imidazolidinone. This epoxy resin is especially suited to electronic material sealing applications.

[0016] The amount of the aprotic polar solvent used is 5 to 200%, and preferably, 10 to 100% of the weight of the epihalohydrin. Besides adding the above-mentioned solvents, the reaction proceeds readily by adding an alcohol-methanol or ethanol. Moreover, toluene, xylene, and the like may be used. The amount of the hydrolyzable halogen here can be measured by, e.g., charging dioxane with the epoxy resin and titrating this with a KOH/ethanol solution while refluxing it for several minutes.

[0017] A quaternary ammonium salt, such as tetramethyl ammonium chloride, tetramethyl ammonium bromide or trimethylbenzyl ammonium chloride, is used as the solvent and reacted for 1 to 10 hours at 50 to 150°C with the mixture of the phenol aralkyl resin and an excess amount of epihalohydrin, a solid or aqueous solution of the alkaline metal hydroxide, such as sodium hydroxide or potassium hydroxide, which is added to the resulting halohydrin ether of the resulting phenol aralkyl resin, then allowed to react again for 1 to 10 hours at 20 to 120°C to close the halohydrin ether ring and obtain the epoxy resin of the present invention. In this case, the amount of the quaternary ammonium salt used normally is 0.001 to 0.2, and preferably, 0.05 to 0.1 mole per equivalent of hydroxyl groups in the phenol mixture. The amount of the alkaline metal hydroxide used normally is 0.8 to 1.5, and preferably, 0.9 to 1.1 moles per equivalent of hydroxyl groups in the phenol aralkyl resin.

[0018] Normally, these reaction products are reacted again by washing with water, and/or subsequently removing the excess amount of epihalohydrin, solvent, and the like without washing with water under heating and reduced pressure and adding an aqueous solution of an alkaline metal hydroxide, such as sodium hydroxide or potassium hydroxide, whereby the epoxy resin of the present invention having a low hydrolyzable halogen concentration can be obtained. In this case, the amount of the alkaline metal hydroxide used normally is 0.01 to 0.2, and preferably, 0.05 to 0.1 mole per equivalent of hydroxyl groups in the phenol aralkyl resin. The reaction temperature normally is 50 to 120°C and the reaction time normally is 0.5 to 2 hours.

[0019] After the reaction, the salt by-product is removed by filtration, washed with water, and the like, and then the solvent, such as toluene or methyl isobutyl ketone, is distilled off under heating and reduced pressure, whereby the epoxy resin of the present invention having a low hydrolyzable halogen concentration can be obtained.

[0020] In the $^{13}\text{C-NMR}$ spectrum of the epoxy resin of the present invention, the peak existing at 35 to 37 ppm means that the position on the aromatic ring where the methylene group is bonded is an ortho-site with respect to a 2,3-epoxypropoxy group. In addition, the peak existing at 40 to 42 ppm means that the position on the aromatic ring where the methylene group is bonded is a para-site with respect to a 2,3-epoxypropoxy group.

[0021] The epoxy resin of the present invention, where the ratio A/B of the integrated value A of the peak existing at 35 to 37 ppm and the integrated value B of the peak existing at 40 to 42 ppm is at least

1.45, both in the $^{13}\text{C-NMR}$ spectrum, and the softening point is at least 63°C , is preferred from the standpoint of solvent solubility.

[0022] The epoxy resin composition of the present invention will now be described. The epoxy resin composition of the present invention may be used singly or by jointly using it with another epoxy resin. When it is used jointly, the proportion of the epoxy resin of the present invention occupying the entire epoxy resin is preferably at least 30 wt.%, and in particular, preferably at least 40 wt.%.

[0023] Polycondensation products of bisphenol A, bisphenol F, bisphenol S, fluorine bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]4,4'-diol, hydroquinone, resorcine, naphthalenediol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis

(4-hydroxyphenyl)ethane, a phenol (phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, dihydroxynaphthalene, etc.), formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4'-bis(chloromethyl)benzene or 1,4'-bis(methoxymethyl)benzene; and a halogenated bisphenol, such as tetrabromobisphenol A, a solid or liquid epoxy resin, such as a glycidyl etherified product derived from an alcohol, cyclic epoxy resin, glycidyl amine-based epoxy resin or glycidyl ester-based epoxy resin, are cited for other epoxy resins which can be used jointly with the epoxy resin of the present invention.

But the present invention is not limited to these compounds, and they can be used singly, or two or more of them can be used.

[0024] The epoxy resin composition in the preferred embodiments thereof of the present invention contains a curing agent. An amine-based compound, acid anhydride-based compound, amide-based compound, phenol-based compound, and the like are cited as examples of curing agents. Although diaminodiphenyl methane, diethylene triamine, triethylene tetramine, diaminodiphenyl sulfone, isophorone diamine, dicyandiamide, a polyamide resin synthesized from a dimer of linolenic acid, phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyl tetrahydrophthalic anhydride, methylnadic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, bisphenol A, bisphenol F, bisphenol S, fluorene bisphenol, terpene diphenol, 4,4'-biphenol, 2,2'-biphenol, 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diol, hydroquinone, resorcine, naphthalene diol, tris-(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, a phenol (phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, dihydroxynaphthalene, etc.), formaldehyde, acetaldehyde, benzaldehyde, p-hydroxybenzaldehyde, o-hydroxybenzaldehyde, p-hydroxyacetophenone, o-hydroxyacetophenone, dicyclopentadiene, furfural, 4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 1,4'-bis(chloromethyl)benzene or 1,4'-bis(methoxymethyl)benzene; and a halogenated bisphenol, such as tetrabromobisphenol A, imidazole, BF_3 -amine complexes, guanidine derivatives, and the like are cited as specific example of the curing

agent which can be used, the present invention is not limited thereto. These curing agents may be used singly, or two or more of them may be used.

[0025] The amount of the curing agent used in the epoxy resin composition of the present invention is preferably 0.5 to 1 equivalents, and in particular, preferably, 0.6 to 1.2 equivalents per equivalent of epoxy groups in the epoxy resin. When the amount per equivalent of epoxy groups is less than 0.5 equivalents or it exceeds 1.5 equivalents, there is the risk in either case that curing will be incomplete or satisfactory curing physical properties will not be obtained.

[0026] In addition, a curing accelerator may be used jointly while employing the above-mentioned curing agent. An imidazole, such as 2-methyl imidazole, 2-ethyl imidazole, 2-phenyl imidazole or 2-ethyl-4-methyl imidazole; a tertiary amine, such as 2-(dimethylaminomethyl)phenol, triethylene diamine, triethanolamine or 1,8-diazabicyclo(5,4,0)undecene-7; an organic phosphine, such as triphenyl phosphine, diphenyl phosphine or tributyl phosphine; a metal compound, such as tin octylate; a tetra-substituted phosphonium tetra-substituted borate, such as tetraphenyl phosphonium tetraphenyl borate or tetraphenyl phosphonium ethyltriphenyl borate; a tetraphenyl boron salt, such as 2-ethyl-4-methylimidazole tetraphenylborate or N-methylmorpholine tetraphenylborate; and the like are cited as examples of the curing accelerator which can be used. The amount of the curing accelerator that is used is 0.01 to 15 weight parts, as needed, per 100 weight parts epoxy resin.

[0027] Furthermore, various compounding agents, such as inorganic fillers, silane coupling materials, mold releases, and pigments, and various thermosetting resins may be added, as needed, to the epoxy resin composition of the present invention. Although powdered crystalline silica, fused silica, alumina, zirconium calcium silicate, calcium carbonate, silicon carbide, silicon nitride, boron nitride, zirconia, fosterite, steatite, Spinel, titania, talc, and the like, or beads obtained by subjecting these powders to spherization, and so forth are cited for inorganic fillers, the present invention is not limited thereto. These fillers can be used singly, or two 2 or more of them can be used. These fillers are preferably used at a proportion occupying 50 to 90 wt. % of the epoxy resin composition, from the standpoint of the heat resistance, moisture resistance, mechanical properties, etc. /5

[0028] The epoxy resin composition of the present invention is obtained by homogeneously mixing the above-mentioned respective constituents. The epoxy resin composition of the present invention can be made into a cured product thereof easily in the same method as a conventionally-known method. For example, the epoxy resin composition of the present invention is obtained first by sufficiently mixing the epoxy resin and curing agent of the present invention, and if necessary, a curing accelerator, inorganic filler, compounding agent, and various thermal setting resins by using, as needed, an extruder, kneader, rolls, and the like, and molding this epoxy resin composition in a melt injection molding method, transfer molding method, injection molding method, compression molding method, and the like by heating it normally to 80 to 200°C for 2 to 10 hours to obtain the cured

product of the present invention.

[0029] In addition, since a crystal with superior solvent solubility is not produced, the epoxy resin of the present invention can be used suitably as an adhesive for laminate boards and the like by making a varnish upon dissolving the epoxy resin composition of the present invention in a solvent. In this case, the cured product is obtained by dissolving the epoxy resin composition of the present invention in a solvent, such as toluene, xylene, acetone, methyl ethyl ketone, methylisobutyl ketone, dimethyl formamide, ethylene glycol monomethyl ether and N-methyl-2-pyrrolidone, impregnating a base material, such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, alumina fibers, or paper therewith, heating and drying this, and hot press-molding the resultant prepreg. A sheet, which will be described later, can be obtained by dissolving the prepreg in a γ -butyrolactone; an amide solvent, such as N-methyl pyrrolidone (NMP), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide or N,N-dimethyl imidazolidilone; a sulfone, such as tetramethylene sulfone; an ether-based solvent, such as diethylene glycol diethyl ether, diethylene glycol diethyl ether, propylene glycol, propylene glycol monomethyl ether, propylene glycol monomethyl ether monoacetate or propylene glycol monobutyl ether; a ketone-based solvent, such as methyl ethyl ketone or methyl isobutyl ketone; or an aromatic solvent, such as toluene or xylene. In the case of prepreg applications, the solvent in this case normally is used in an amount 10 to 70 wt.%, and preferably, 15 to 70 wt.% of mixtures of the epoxy resin composition of the present invention and the various solvents. In addition, in the case of sheet applications, the solvent is used in

an amount where the solid content concentration in the varnish normally is 10 to 80 wt.%, and preferably, 20 to 70 wt.%.

[0030] When the above-mentioned varnish is used to turn it into a sheet shape, this varnish is used by coating it so that the thickness after it dries on the base material is a prescribed thickness, e.g., 5 to 100 μm , and subsequently drying it in various coating methods, such as a known gravure coating method per se, screen printing, metal masking method or spin coating method. However, which coating method is used is suitably selected depending on the type, shape and size of the base material and the thickness of the paint film. The base material is, e.g., a film fabricated from various polymers and/or copolymers thereof, such as polyamide, polyamide imide, polyallylate, polyethylene terephthalate, polybutylene terephthalate, polyether ether ketone, polyether imide, polyether ketone, polyketone, polyethylene and polypropylene; or a metal foil, such as copper foil, and in particular, preferably, a polyimide film and copper foil. When a release film is used, it is used as a bonding sheet. A "bonding sheet" is a release film coated with an adhesive layer (of varnish) on one side and then pasted to another release agent to be used as an adhesive material while pasting a flexible printed wiring board to another flexible printed wiring board. A sheet-like cured product can be obtained by heating the sheet obtained in this way.

[0031] [Practical Examples]

The present invention will now be described in further detail according to the practical examples, but the present invention is not limited to these practical examples. Moreover, the epoxy equivalent, softening point

and melt viscosity were measured at the conditions below.

-Epoxy equivalent

This is measured in accordance with JIS K 7236 and the unit is g/eq.

-Softening point

This was measured in a method according to JIS K 7234.

-Melt viscosity

The melt viscosity in a cone and plate method at 150°C

Measurement instrument: Cone and plate (ICI) high-temperature viscometer
(made by Research Equipment (London) Ltd.)

No. 3 cone: (measurement range: 0 to 2.00 Pa-s)

Amount of sample: 0.15±0.01g

[0032] Synthesis Example 1

A four-neck flask equipped with a stirrer, thermometer and condenser is charged with 382 parts phenol, 485 parts 4,4'-bis(methoxymethyl)-1,1'-biphenyl, and 8 parts p-toluene sulfonic acid hydrate and allowed to react for 4 hours while maintaining the reaction temperature at 125°C. The methanol generated thereduring was distilled off outside the reaction system. After the reaction finished, 1,500 parts methyl isobutyl ketone (MIBK) were added and repeatedly washed with water. Next, 615 parts of a phenol aralkyl resin P1 were obtained by distilling off the unreacted phenol and MIBK. The softening point of the resultant phenol aralkyl resin P1 was 92°C, the melt viscosity was 0.91 Pa-s, and the hydroxyl group content was 223 g/eq.

[0033] Synthesis Example 2

Except for changing the 382 parts of the phenol in Synthesis Example 1 to 430 parts, the same operation as in Synthesis Example 1 was performed to obtain 726 parts of a phenol aralkyl resin P2. The softening point of the resultant phenol aralkyl resin P2 was 85°C, the melt viscosity /6 was 0.47 Pa-s, and the hydroxyl group content was 220 g/eq.

[0034] Synthesis Example 3

Except for changing the 382 parts of the phenol in Synthesis Example 1 to 478 parts, the same operation as in Synthesis Example 1 was performed to obtain 620 parts of a phenol aralkyl resin P3. The softening point of the resultant phenol aralkyl resin P3 was 82°C, the melt viscosity was 0.35 Pa-s, and the hydroxyl group content was 215 g/eq.

[0035] Synthesis Example 4

Except for changing the 382 parts of the phenol in Synthesis Example 1 to 506 parts, the same operation as in Synthesis Example 1 was performed to obtain 632 parts of a phenol aralkyl resin P4. The softening point of the resultant phenol aralkyl resin P4 was 79°C, the melt viscosity was 0.25 Pa-s, and the hydroxyl group content was 212 g/eq.

[0036] Synthesis Example 5

Except for changing the 382 parts of the phenol in Synthesis Example 1 to 573 parts, the same operation as in Synthesis Example 1 was performed to obtain 611 parts of a phenol aralkyl resin P5. The softening point of the resultant phenol aralkyl resin P5 was 74°C, the melt viscosity was 0.15 Pa-s, and the hydroxyl group content was 211 g/eq.

[0037] Synthesis Example 6

Except for changing the 382 parts of the phenol in Synthesis Example 1 to 611 parts, the same operation as in Synthesis Example 1 was performed to obtain 615 parts of a phenol aralkyl resin P6. The softening point of the resultant phenol aralkyl resin P6 was 71°C, the melt viscosity was 0.12 Pa-s, and the hydroxyl group content was 207 g/eq.

[0038] Synthesis Example 7

A four-neck flask equipped with a stirrer, thermometer and condenser was charged with 955 parts phenol, 1,256 parts 4,4'-bis(chloromethyl)-1,1'-biphenyl, and 10 parts p-toluene sulfonic acid hydrate and allowed to react for 1.5 hours at 50°C, for 1 hour at 70°C, and for 2 hours at 80°C. After the reactions were finished, 2,500 parts MIBK were added and washing with water was repeated. Next, 1,457 parts of a phenol aralkyl resin P7 were obtained by distilling off the unreacted phenol and the MIBK from the oil layer by heating under reduced pressure. The softening point of the resultant phenol aralkyl resin P7 was 82°C, the melt viscosity was 0.40 Pa-s, and the hydroxyl group content was 221 g/eq.

[0039] Synthesis Example 8

Except for changing the 955 parts of the phenol in Synthesis Example 7 to 1,481 parts, the same operation as in Synthesis Example 7 was performed to obtain 1,729 parts of a phenol aralkyl resin P8. The softening point of the resultant phenol aralkyl resin P8 was 71°C, the melt viscosity was 0.12 Pa-s, and the hydroxyl group content was 207 g/eq.

[0040] Practical Example 1

925 parts epichlorohydrin and 185 parts dimethyl sulfoxide were added to 446 parts of the resin P1 obtained in Synthesis Example 1 and dissolved, subsequently heated to 45°C, 82 parts flaky sodium hydroxide (purity: 99%) were added over 90 minutes, and subsequently allowed to react for 2 hours at 45°C and 0.5 hours at 70°C. Washing with water was repeated next to restore the solution to neutral, and the excess epichlorohydrin was distilled off from the oil layer under heating and reduced pressure, while 115 parts MIBK were added to and dissolved in the residue. Furthermore, this MIBK solution was heated to 70°C, 27 parts of a 30 wt.% aqueous sodium hydroxide solution were added thereto and allowed to react for 1 hour, after which washing with water was repeated to restore the neutrality. 475 parts of an epoxy resin E1 of the present invention were obtained by distilling off the MIBK from the oil layer under heating and reduced pressure. The $^{13}\text{C-NMR}$ spectrum ($\text{CDCl}_3, 300\text{MHz}$) of the resultant epoxy resin E1 is shown in Figure 1.

[0041] Practical Example 2

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 439 parts of the resin P2 obtained in Synthesis Example 2, the same operation as in Practical Example 1 was performed to obtain 474 parts of an epoxy resin E2 of the present invention.

[0042] Practical Example 3

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 430 parts of the resin P3 obtained in Synthesis Example 3, the same operation as in Practical Example 1 was

performed to obtain 502 parts of an epoxy resin E3 of the present invention.

[0043] Practical Example 4

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 424 parts of the resin P3 obtained in Synthesis Example 3, the same operation as in Practical Example 1 was performed to obtain 493 parts of an epoxy resin E4 of the present invention.

[0044] Comparative Example 1

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 425 parts of the resin P5 obtained in Synthesis Example 5, the same operation as in Practical Example 1 was performed to obtain 492 parts of epoxy resin E5 for comparison.

[0045] Comparative Example 2

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 414 parts of the resin P6 obtained in Synthesis Example 6, the same operation as in Practical Example 1 was performed to obtain 500 parts of epoxy resin E6 for comparison.

[0046] Comparative Example 3

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 442 parts of the resin P7 obtained in Synthesis Example 7, the same operation as in Practical Example 1 was performed to obtain 540 parts of an epoxy resin E7 for comparison.

[0047] Comparative Example 4

Except for changing the 446 parts of the resin P1 obtained in Synthesis Example 1 in Practical Example 1 to 414 parts of the resin P8 obtained in Synthesis Example 8, the same operation as in Practical Example 1

was performed to obtain 500 parts of an epoxy resin E8 for comparison.

[0048] The physical properties of the epoxy resins of the present invention obtained in the above practical examples and comparative examples and the epoxy resins for comparison are shown in Tables 1 and 2.

[0049] Table 1

	実施例1	実施例2	実施例3	実施例4
エポキシ当量(g/eq)	289	291	286	278
軟化点(°C)	79	73	68	65
溶融粘度(Pa·s)	0.79	0.45	0.27	0.22
A/B	1.83	1.76	1.63	1.50

Key:

	Practical Example 1	Practical Example 2	Practical Example 3	Practical Example 4
Epoxy equivalent (G/eq)	1	2	3	4
Softening point (°C)				
Melt viscosity (Pa·s)				
A/B				

[0050] Table 2

	比較例1	比較例2	比較例3	比較例4
エポキシ当量(g/eq)	278	278	295	278
軟化点(°C)	61	58	71	58
溶融粘度(Pa·s)	0.14	0.10	0.37	0.11
A/B	1.54	1.33	1.21	0.95

Key:

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Epoxy equivalent (G/eq)				
Softening point (°C)				
Melt viscosity (Pa·s)				
A/B				

[0051] Test Examples 1 to 8

The epoxy resins E1 to E4 obtained in Practical Examples 1 to 4 and the epoxy resins E5 to E8 obtained in Comparative Examples 1 to 4 were dissolved in methyl ethyl ketone used as the solvent so that the resin

concentration was 70 wt.%, and stored in a 5°C environment. The results of the test are shown in Table 3 (in order of the resins obtained in Practical Examples 1 to 4 from left to right) and Table 4 (in order of the resins obtained in Comparative Examples 1 to 4 from left to right). Moreover, the criteria are shown below.

○: No crystal deposited even after 1 week or more elapsed.

×: A crystal deposited within 1 week.

[0052] Table 3

エポキシ樹脂 試験結果	試験例1 E1	試験例2 E2	試験例3 E3	試験例4 E4
	○	○	○	○

Key:

	Test Example 1	Test Example 2	Test Example 3	Test Example 4
Epoxy resin test results				

[0053] Table 4

エポキシ樹脂 試験結果	試験例6 E5	試験例7 E6	試験例8 E7	試験例9 E8
	×	×	×	×

Key:

	Test Example 1	Test Example 2	Test Example 3	Test Example 4
Epoxy resin test results				

[0054] In addition, the A/B and softening points of the epoxy resins E1 to E4 obtained in Practical Examples 1 to 4 and the epoxy resins E5 to E8 obtained Comparative Examples 1 to 4 were graphed, as shown in Figure 2. The epoxy resins of the present invention wherein the A/B and the softening points of the above-mentioned test examples and comparative test examples fall in the specified ranges show more satisfactory solvent resistance

than that of the epoxy resins outside those ranges.

[0055] Practical Example 6

The epoxy resin E2 obtained in Practical Example 2, a phenol novolak resin (PN-80: made by Nippon Kayaku Co., Ltd.; hydroxyl group equivalent: 105 g/eq; softening point: 86°C), as the curing agent, 2-ethyl-4-methyl imidazole (2E4MZ), as the curing accelerator, and methyl ethyl ketone (MEK) and methyl cellosolve (MCS), as the diluents, were compounded at the weight proportions shown in the "Compounding" column in Table 5 to prepare varnishes. Using these varnishes, a glass cloth (WEA18W105F115N: made by Nitto Boseki Co., Ltd.) was impregnated therewith, and subsequently dried for 7 minutes using a 120°C hot air dryer to obtain a semicured prepreg. Eight 8 pieces of the above-mentioned prepreg and a piece of copper foil (JTC foil made by Nikko Gould Foil Co., Ltd.; 35 µm) were superpositioned, and this was heated, pressurized and molded for 60 minutes at a temperature of 170°C and 40 kgf/cm² to fabricate a glass cloth laminate board. The physical properties of the resultant laminate board were measured according to the following criteria and methods. The measurement results are shown in Table 5.

-Glass transition temperature

Thermal mechanical analyzing apparatus (TMA): Shinko Riku K.K. TM-7000

Rate of temperature rise: 2°C/min.

-Copper foil peel test

Tensile tester: Tensilon RTM-500, made by Toyo Baldwin. Co. Ltd.

Tensile mode: 180°C peel

Crosshead speed: 200 mm/min.

Measurement temperature: 30°C

-Water absorption factor

Testpiece: 5 cmx5 cm

Amount of increase in weight (wt.%) after boiling for 24 hours in 100°C hot water

-Dielectric constant

Measured under JIS 6481

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[0056] Comparative Example 6

A brominated bisphenol A epoxy resin (Epomick R-232, made by Mitsui Chemicals, Inc.; epoxy equivalents: 483 g/eq), as the epoxy resin, a phenol novolak resin (PN-80: made by Nippon Kayaku Co., Ltd.; hydroxyl group equivalent: 105 g/eq; softening point: 86°C), as the curing agent, 2-ethyl-4-methyl imidazole (2E4MZ), as the curing accelerator, and methyl ethyl ketone (MEK) and methyl cellosolve (MCS), as the diluents, were compounded at the weight proportions shown in the "Compounding" column in Table 5 to prepare varnishes. The rest of the operation was performed as in Practical Example 6. The measurement results are shown in Table 5.

[0057] Table 5

	実施例6	比較例6
(配合)		
E2	100	
R-232		100
PN-80	36	22
2E4MZ	0.3	0.3
MEK	82	73
MCS	9	8
(硬化物性)		
ガラス転移温度(℃)	140	125
鏡面剥離強度(kN/m)	2.8	1.9
吸水率(%)	0.6	0.5
誘電率	4.6	4.8

Key for Table 5:

	Practical Example 6	Comparative Example 6
(Compounding)		
E2		
R-232		
PN-80		
2E4MZ		
MEK		
MCS		
(Cured physical properties)		
Glass transition temperature (°C)		
Copper foil peel test (kN/m)		
Water absorption factor (%)		
Dielectric constant		

[0058] According to Table 5, the cured product of the present invention has far superior heat resistance, close adhesiveness and water resistance and lower dielectric properties than the bisphenol A epoxy resin used in general in the past.

[0059] [Advantages of the Invention]

The cured product of the epoxy resin composition having the epoxy resin of the present invention has outstanding heat resistance, close adhesiveness, moisture resistance and dielectric properties. As a consequence, it is very useful when it is employed in various composite materials, adhesives, paints, and the like including insulation materials for electrical and electronic parts, laminate boards (printed wiring boards, etc.) and CFRPs.

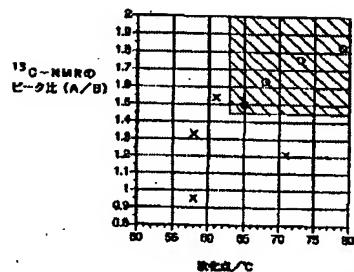
[Brief Description of the Drawings]

[Figure 1] A ^{13}C -NMR spectrum of the epoxy resin of the present invention obtained in Practical Example 1. The Y axis in Figure 1 represents the absorption intensity and the X axis represents ppm, respectively.

[Figure 2] A graph of the relation between the ratio A/B of the integrated value A of the peak present at 35 to 37 ppm in the ^{13}C -NMR spectrum of

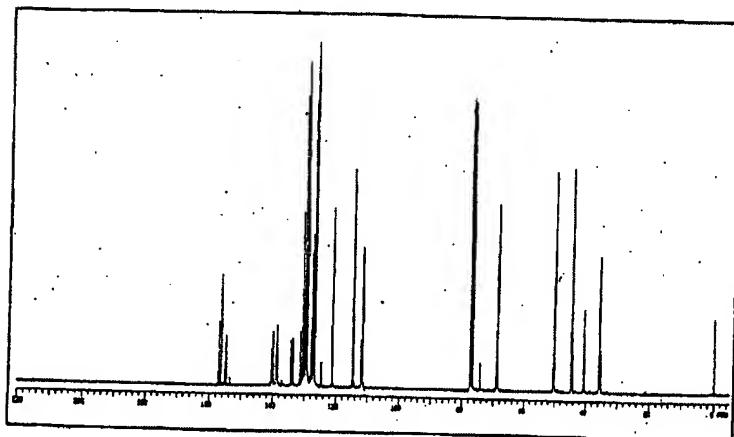
the epoxy resin of the present invention and the epoxy resin for comparison and the integrated value B of the peak present at 40 to 42 ppm. The o symbol represents the epoxy resins E1 to E4 of the present invention and x symbol represents the epoxy resins E5 to E8 for comparison. The epoxy resins of the present invention are present in the diagonal part.

[Figure 2]



Key: (Y axis) ^{13}C -NMR peak ratio A/B; (X axis) Softening point °C

[Figure 1]



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